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Fabrication of oriented $L1_0$ -FePt and FePd nanoparticles with large coercivity

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Oriented $L1_0$ -FePt and FePd nanoparticles with coercivities as large as 5 kOe (FePt) and 3 kOe (FePd) were fabricated by alternating deposition of Pt(or Pd) and Fe nanoparticles and their annealing at the temperatures between 773 and 873 K on single crystal NaCl and MgO. Atomic ordering reactions and degrees of order towards the $L1_0$ -structure formation in these nanoparticles were investigated by high resolution electron microscopy and electron diffraction, and magnetic coercivities at low temperature were also measured. The long range order parameter of the FePt nanoparticles was ~ 0.56 even after annealing at 873 K for 24 h. The coercivity of the FePt nanoparticles at 100 K was as high as twice the room temperature value. The low degree of order in the $L1_0$ -structure formation and the thermal effect on magnetization have been found in the present FePt and FePd nanoparticles. These are closely concerned with the origin of the coercivity values which are very small in comparison with those expected from the single magnetic domain theory. © 2002 American Institute of Physics. [DOI: 10.1063/1.1456446]

I. INTRODUCTION

Since $L1_0$ -type FePt and CoPt ordered alloy nanoparticles exhibit a large coercivity owing to the rotation magnetization¹ which originates from the single magnetic domain nature, they have attracted much interest as one of the candidates for future high-density magnetic storage media. The structures of FePt and CoPt have high magnetoanisotropies^{2,3} which enable these particles to overcome the thermal fluctuation of the magnetic moments. The magnetocrystalline anisotropies of these alloys are closely related to the atomic long-range order parameter. These ordered alloys have their easy axes of magnetization along their crystallographic c -axes. From the technological viewpoints for better hard magnetic properties, the easy axis orientation of the ordered particles should be controlled. Recently, one of the attempts to control the easy axis orientation has been made taking advantage of the epitaxial growth of FePt (Refs. 4 and 5) and FePd (Ref. 6) nanoparticles on NaCl and MgO single crystalline substrates. These nanoparticles exhibited high coercivities as large as 3–5 kOe after annealing at 873 K, but are still not large as the single magnetic domain theory¹ predicts. One possible reason is that in these nanoparticles atomic ordering reaction towards the $L1_0$ -structure with the large magnetocrystalline anisotropy is still not enough even under the annealing temperature of $\sim 0.4T_m$, where T_m is the melting temperature of alloy. Another possible reason is that the size of these FePt and FePd nanoparticles as small as 10 nm is already close to the size limit for the superparamagnetic behavior. The third possible reason is that the magnetocrystalline anisotropy of these nanoparticles differ largely from those of the bulk specimens. In order to know the reason for the coercivity values of these

$L1_0$ -type nanoparticles, atomic ordering reactions towards the $L1_0$ -structure formation in these nanoparticles were investigated in the present study using high resolution electron microscopy (HREM) and electron diffraction, and also, the magnetic coercivities at room and low temperatures were measured.

II. EXPERIMENT

The specimens were fabricated by the electron beam evaporation technique. The process took advantage of the overgrowth of Fe particles onto the Pt or Pd seed particles which were epitaxially grown initially on the NaCl(001) or MgO(001) substrates. The substrates were kept at 673 K during the deposition. Because of the epitaxial relation between Pt (or Pd) and bcc-Fe, a mutual fixed orientation exists among Fe nanoparticles with respect to the seed Pt (or Pd) particles. Amorphous Al_2O_3 film was further deposited to protect the Fe particles from oxidation. Annealing of these specimens for the formation of ordered nanoparticles were made in a vacuum furnace at temperatures between 773–873 K for 1, 6, and 24 h, with the heating and cooling rates of about 5 and 10 K/min, respectively. Details of fabrication method are referred to in our previous works.^{4–6} The composition analysis of the specimens was done by energy dispersive x-ray spectroscopy (EDS). Specimen characterization was performed by HREM and their magnetic properties were measured by a SQUID magnetometer.

III. RESULTS AND DISCUSSION

A. Magnetic properties

Table I shows the mean composition, coercivity, mean particle size, and annealing condition for the fabricated FePt and FePd nanoparticles. Both FePt and FePd have nonstoichiometries and their T_c varies with composition. In the case of FePt and FePd alloys, their maximum T_c 's are

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TABLE I. Coercivity, mean particle size, and annealing condition of oriented FePt and FePd nanoparticles with compositions. These particles were deposited on single crystal NaCl and MgO substrate with quasi-two-dimensional dispersion. \parallel and \perp mean the magnetic field direction parallel to and normal to the film plane, respectively.

Composition	Coercivity/kOe	Size/nm	Annealing
50 at. % Pt	5(\parallel)	12	873 K-6 h
52 at. % Pt	0.38(\perp), 0.45(\parallel)	14	843 K-1 h
56 at. % Pt	1.8(\perp), 1.7(\parallel)	12	873 K-1 h
56 at. % Pt	5.5(\perp), 4.6(\parallel)	12	873 K-24 h
49 at. % Pd	0.6(\perp), 0.28(\parallel)	10	773 K-1 h
58 at. % Pd	1.2(\perp), 0.3(\parallel)	10	773 K-1 h
58 at. % Pd	3.3(\perp), 2.4(\parallel)	10	873 K-1 h

obtained⁷ at the compositions of Fe-50 at. % Pt and Fe-58 at. % Pd, respectively. Within the same alloying system and under the same annealing condition, the rate of atomic ordering of the specimen with the higher T_c becomes larger than that of the specimen with the lower T_c . In the present study, a coercivity of 5 kOe was obtained after annealing at 873 K for 6 h in the case of the Fe-50 at. % Pt specimen, while at 873 K for 24 h in the case of Fe-56 at. % Pt. Coercivities of FePd specimens show a similar tendency with respect to the composition-annealing condition relation (see Table I). In order to know the contribution of thermal effect on the coercivity of the nanoparticles, the magnetic hysteresis was measured using SQUID at low temperatures down to 100 K. The ratio of the low and the room temperature coercivity values, $H_c(100\text{ K})/H_c(300\text{ K})$ was 1.8 for the FePt (60 at. % Pt; annealed at 873 K-24 h) nanoparticle-films. This result means that the thermal effect on the coercivity of these nanoparticles is fairly large.

B. HREM and electron diffraction studies

It is important to note that the huge coercivity expected from the single magnetic domain theory for the $L1_0$ -type magnetic alloy small particles is only attainable when the atomic long-range order of the $L1_0$ -type structure in the alloy nanoparticles is satisfied. So, it is very important to examine whether the ordering reactions are fulfilled or not in the nanoparticles under the annealing conditions. Figure 1(a) shows an example of the HREM image of the nanoparticle of Fe-52 at. % Pt specimen annealed at 843 K for 1 h. In this case, the annealing of the specimen film was made in a high vacuum on the NaCl substrate. Such a local structure of the $L1_0$ -type lattice in the form of three variant domains with three orthogonal c -axes parallel to the three principal axes of the NaCl substrate as seen in Fig. 1(a) started to appear on annealing at 773 K for 1 h and grew at 843 K, which gave an electron diffraction pattern with diffuse intensities at 001 and 110 reciprocal lattice points [Fig. 1(b)]. When the annealing temperature increased up to 873 K, the structure with the three variant domains became clearer as shown in Fig. 2(a) (after 6 h annealing), and the superlattice spots also became stronger as seen in Fig. 2(b). The three variant domain structure changed into single variant structure after a prolonged annealing (873 K for 24 h).⁸ The particle edge-to-edge dis-

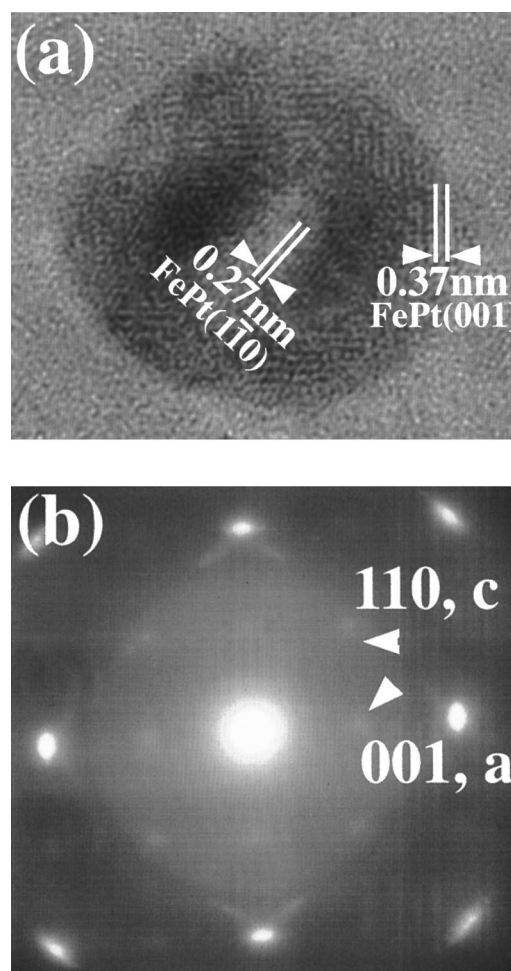


FIG. 1. HREM image (a) and the corresponding SAED pattern (b) of Fe-52 at. % Pt nanoparticles after annealing at 843 K for 1 h. {001} and {110} lattice fringes in the particles indicate the locally ordered regions.

tance was 5–10 nm for these 10 nm-sized FePt nanoparticles. During the annealing, a partial coalescence occurred for FePt. Some close particles coalesced, but a size distribution little changed during the annealing below 873 K. Above 923 K, the coalescence became fluent. The particle size and the interparticle distance of FePd nanoparticles were similar to those of the FePt nanoparticles.

The long-range order parameter was calculated from the electron diffraction intensity ratios of I_{110}/I_{220} and I_{001}/I_{002} for this specimen annealing at 873 K for 24 h by exciting both the $hh0$ and $00l$ systematic reflections independently. The obtained averaged long-range order parameter was 0.56. It is, therefore, understood that the atomic ordering reaction in the nanoparticles can not be fulfilled even after the annealing at 873 K for 24 h. It is generally understood that the long-range order parameter (S) largely affects the value of uniaxial magnetocrystalline anisotropy constant (K_u). According to Maykov *et al.*,⁹ a relation $K_u \propto S^2$ was derived. A similar tendency was found also in the case of FePd nanoparticles.

From the above experiments, it has been demonstrated that rather lower coercivity values of the FePt and FePd nanoparticles in comparison with those expected from the single magnetic domain theory of small particles is mainly

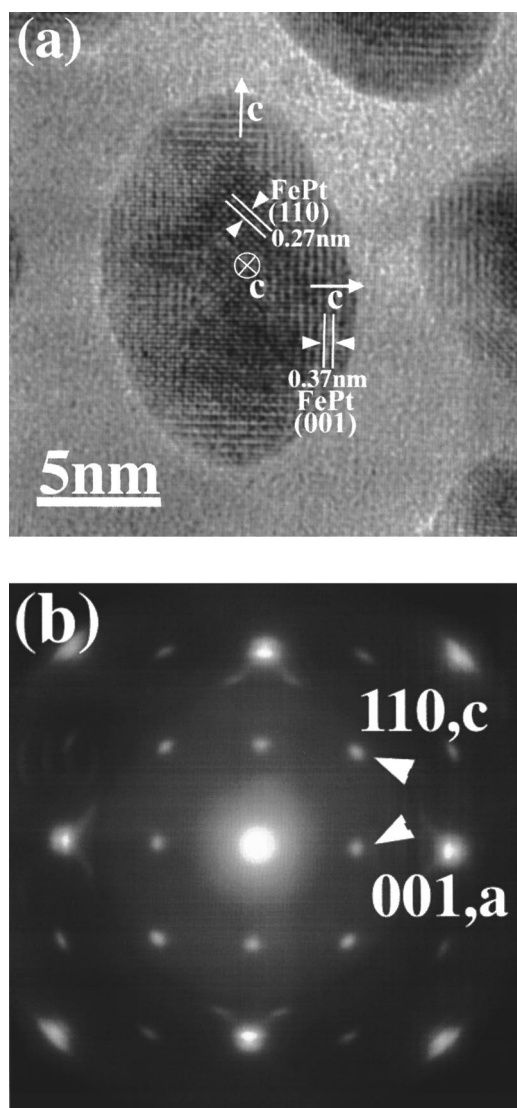


FIG. 2. HREM image (a) and the corresponding SAED pattern (b) of Fe-56 at.% Pt nanoparticles after annealing at 873 K for 6 h. A three variant domain structure is clearly seen in the particle.

attributed to both the low degree of atomic order in the $L1_0$ lattice and also the thermal effect on the coercivity.

C. Atomic ordering and magnetic coercivity

Coercivities of both FePt and FePd nanoparticles were enhanced as the ordering reaction proceeded. T_c of FePt is higher than that of FePd, so the ordering energy (ν) of FePt must be larger than that of FePd. However, according to our annealing study,⁶ coercivity of FePd started to increase after annealing at 773 K, while in the case of FePt, higher annealing temperatures above 873 K were necessary to obtain a sufficiently large coercivity more than 1 kOe. This inconsistency is presumed to arise from the difference in vacancy concentrations between FePt and FePd at the same temperature. The melting temperatures of FePt is about 300 K higher than that of FePd, indicating that the vacancy concentration in FePd is higher than that in FePt under the temperature of

773 K. The rate of atomic diffusion in atomic ordering of FePt and FePd have to be compared by using a parameter T/T_m but not by the annealing temperature T . The parameter T/T_m is based on an idea that the vacancy concentration takes a maximum value at melting temperature. From this viewpoint, the annealing temperatures of 773 K for FePd and 873 K for FePt both correspond to about $0.4 T_m$. So we can conclude that the difference in vacancy concentration between FePt and FePd changes the atomic diffusivity and causes the difference in their annealing temperatures for atomic ordering.

IV. CONCLUSION

$L1_0$ -type FePt and FePd nanoparticles with orientation were fabricated by alternative deposition of Pt (or Pd) and Fe nanoparticles and their annealing at temperatures between 773 and 873 K on single crystal NaCl and MgO. Their coercivities were as large as 5 kOe (FePt) and 3 kOe (FePd). Atomic ordering reactions and degrees of order towards the $L1_0$ -structure formation in these nanoparticles were investigated by HREM and electron diffraction. After annealing at 873 K for 24 h, the averaged value of long-range order parameter of the FePt nanoparticles measured by electron diffraction intensities was 0.56. The contribution of the temperature effect on coercivities was estimated by measuring the coercivity at low temperatures. The coercivity at 100 K was as high as twice the coercivity at room temperature in the FePt nanoparticles. From these results, it can be concluded that the reason for rather low coercivity values of the FePt and FePd nanoparticles in comparison with those expected from the single magnetic domain theory of small particles is attributed to both the low degree of atomic order and the thermal agitation of magnetic moments due to nanoparticles. However, we still have a room to consider the magnitudes of magnetocrystalline anisotropy constants of these nanoparticles which may have smaller values than those of the bulk alloys.

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